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Effect of compounding principles on thermal, mechanical and magnetic performance of soft magnetic polymethylmethacrylate/Fe_3O_4 nanocomposites

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Abstract

In this study, the effect of compounding principles on the properties of Polymer Bonded Soft Magnetic Nanocomposites (PBSMNs) was discussed. The polymethylmethacrylate /Fe_3O_4 magnetic nanocomposites (Fe_3O_4: 30 wt%) were prepared by the *in situ* process based on the solution and spray drying method, as well as by the *ex situ* process based on the kneading machine. As reference, the process combining these two compounding principles was also carried out for the PBSMN preparation, named as *in-between* process. The morphology structures, thermal, mechanical and magnetic properties of the magnetic nanocomposites achieved with different compounding principles were characterized. The results show that compounding principles have significant influence on the properties of the magnetic polymer nanocomposites. In the end, their contributions to the power electronic applications were discussed as well.

Keywords

Polymer composites, soft magnetic composites, *in situ* polymerization, compounding process

Introduction

Nowadays, nanofilled polymer composites have been widely applied for various areas of microsystems, informatic storage, clean energy, aerospace, automobile, chemical catalysis and biomedical, due to their specially resulting mechanical, electronic, magnetic, optical and thermal properties associated with the same magnitude between polymer coils and nanofillers, molecular interaction between the polymer and nanofillers as well as the large surface–volume ratio of nanofillers.[1–5]

Magnetic polymer nanocomposites have been drawing more and more attention because of their fantastic performance in applications of electromagnetic screening devices, magnetic shielding, noise/vibration controlling, especially biology and medical including cell/DNA/RNA separation, site-specific drug delivery etc.[6–8] In the past decades, numbers of approaches on preparing magnetic polymer nanocomposites have been reported, which can be classified as *ex situ* and *in situ* processes. The *ex situ* process is that the magnetic particles and polymer matrix are fabricated separately, and then mixing or compounding together by the kneader, blender or extrusion machine. The *in situ* process means to synthesize the polymer around the particles or embed the particles in the solved polymers. For *ex situ*

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compounding principle, many significant achievements have been presented, but in high filling degree the dispersion of nanoparticles is still poor and agglomeration of them are hardly avoided.[9–11] In contrast, with regard to the dispersion quality of nanoparticles, the *in situ* principles are favorable. Lots of methods have been published about preparing the magnetic/polymer core/shell composites particles, both in microscale and nanoscale, including various emulsion and inverse emulsion polymerization, dispersion and suspension polymerization.[12–16] By those *in situ* processes, the magnetic polymer nanocomposites with super-paramagnetic property were able to achieved, which is difficult to be obtained by *ex situ* principle.[17–18] However, as good magnetic properties were received in high filling contents, how to get the acceptable mechanical properties in further processes, for example, injection molding process becomes more significant. The literature on the study of the correlation between compounding process methods and magnetic polymer composites are quite limited, particularly on comparison of effects of *ex situ* and *in situ* process on magnetic polymer nanocomposites properties.

In this paper, the polymethylmethacrylate (PMMA)/Fe_3O_4 magnetic nanocomposites were prepared by the *in situ* compounding process based on the solution and spray drying method previously reported by authors,[18] the *ex situ* process based on the kneading machine as well as by *in-between* process. The thermal, mechanical and magnetic properties of nanocomposites achieved with three different principles were analyzed and compared.

Experimental

Composites preparation

In situ process. The presented *in situ* process for the preparation of the polymeric magnetite nanocomposites particles is based on the solution process reported in aforementioned literature of authors.[17,18] Its strategy starts with magnetic liquid containing Fe_3O_4 nanoparticles synthesized by an aqueous co-precipitation reaction. The ricinoleic acid adsorbed onto the magnetite particle surface at liquid–liquid interface and hydrophobization was added to stabilize the particle liquid. Meanwhile, the agglomerating particles in the aqueous phase were separated and disintegrated physically and chemically. Then the solved PMMA (preconditioned 4 h, 80°C in advance), was mixed into this stable ferromagnetic liquid. Finally, the solution consisting of PMMA, Fe_3O_4 nanoparticles and the solvent was delivered to a spray tower, where it was atomized and solidified as fine droplets without any segregation due to the high drying velocity. The end produced spray dried PMMA/Fe_3O_4 particles was obtained, which can be processed by injection molding process to manufacture functional parts. In this study, the composite of PMMA(64 wt%)-Fe_3O_4(30 wt%)-ricinoleic acid (6 wt%) was fabricated for further investigation.

Ex situ process. The *ex situ* process was performed in a micro co-twin screw kneader. The Fe_3O_4 nanoparticles were synthesized by the same method as in *in situ* process. With the certain filling fractions equal to *in situ* process, the nanoparticles (30 wt%), ricinoleic acid (6 wt%) and PMMA matrix (64 wt%) were compounded in the kneader. After 25 min compounding at 230°C with rotation speed of 60 rpm, the final composites were collected and granulated for the next step using by injection molding process.

In-between process. Before the *in-between* compounding process, the nanoparticles of Fe_3O_4/ricinoleic acid (wt% ratio 5:1) were produced by the aforementioned *in situ* plus spray drying process without adding PMMA in order to guarantee the comparability with *in situ* and *ex situ* process. Afterwards, the Fe_3O_4/ricinoleic acid powders and PMMA granulates (conditioned 4 h 80°C) with the intending wt% were compounded in the kneader. After 25 min compounding at 230°C with rotation speed of 60 rpm, the final composites with the same filling concentrations as *in situ* and *ex situ* process were obtained.

Characterizations

The crystallography and structures of bare Fe_3O_4 and PMMA/ Fe_3O_4 nanocomposites prepared by different principles were identified by wide angle X-ray diffraction spectrum (WXRD) with Cu Kα radiation ($\lambda = 0.1541$ nm) (Simens D5000, Germany); Fourier transform infrared spectroscopy (FTIR) with potassium bromide is used for the chemical bonds identifications of achieved nanocomposites. The thermal properties of nanocomposites are characterized by differential scanning calorimeter (DSC) and thermal gravity analyzer (TGA) for determining the decomposition temperature and melting temperature. The mechanical properties of the nanocomposites are assessed by tensile tests machine (Zwick) according to the ISO 527 standard procedure in which the tensile test samples were formed by injection molding process. Magnetic properties of the obtained nanomagnetic composites are tested on the basis of the hysteresis curve method at the frequency of 1 Hz.

In order to analyze the dispersion situation of nanoparticles in various compounding methods, the morphology of nano composites are observed by Scanning electronic microscope (SEM).

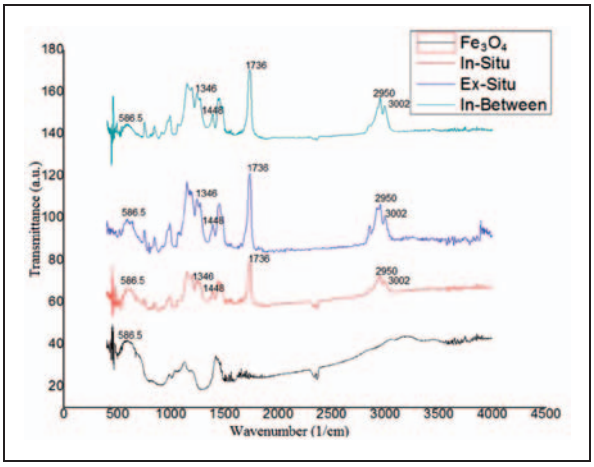

Figure 1. FTIR spectra of the PMMA/Fe_3O_4 composites prepared by different compounding methods.

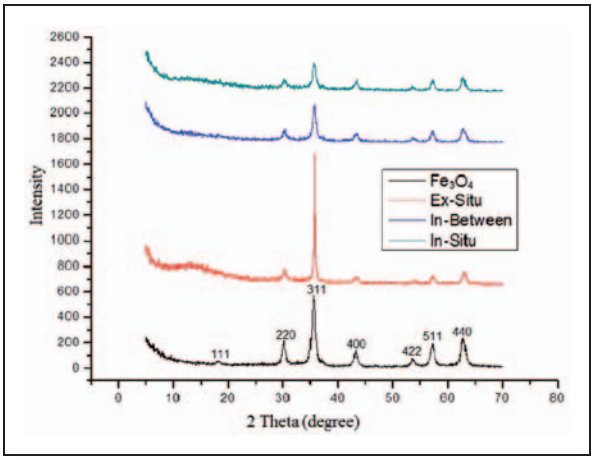

Figure 2. XRD patterns of the PMMA/Fe_3O_4 nanocomposites prepared by different compounding methods.

Results and discussions

Microstructures

The various chemical bonds of the magnetic nanocomposites were characterized by the Fourier transform infrared spectroscopy (FTIR) with potassium bromide. Figure 1 shows the FTIR spectra of PMMA/Fe3O4 nanocomposites by various compounding processes. The testing samples were prepared from the injection molded specimens. According to the results, the adsorption peaks at 586.5 cm^{-1} were the characteristic absorption of Fe O bond, which confirmed the presence of Fe_3O_4 nanoparticles, and it is found in all the three types of PMMA/Fe3O4 nanocomposites. The strong absorption feature peak at 1736 cm^{-1} corresponding to the double CO bond indicates the existence of PMMA in the composites, as well as the several feature peaks in the 3002 cm^{-1} and 2950 cm^{-1} attributed to the stretching of CH bonds of the saturated alkane in PMMA. In addition, the peaks at 1346 cm^{-1} and 1448 cm^{-1} corresponding to deformation vibration of CH_2 and CH_3 also dedicate the existence of PMMA in the composites. However, there is no feature peak of oleic acid at 1716 cm^{-1} appearing in the nanocomposites FTIR measurement results. The reason for that can be that due to the high processing temperature (220°C), the oleic acid is decomposed during the injection molding process of the sample preparation.

In Figure 2, the crystallinity type and size of Fe_3O_4 nanoparticles in nanocomposites are dedicated by wide angle X-ray diffraction spectrum (WXRD). All the diffraction peaks at (111), (220), (311), (400), (422), (511) and (440) are indexed to the cubic spinel phase of Fe_3O_4. The average crystallite size D can be calculated using the Debye–Sherrer formula $D = K\lambda/(\beta\cos\theta)$, where K is Sherrer constant, λ is the X-ray wavelength,

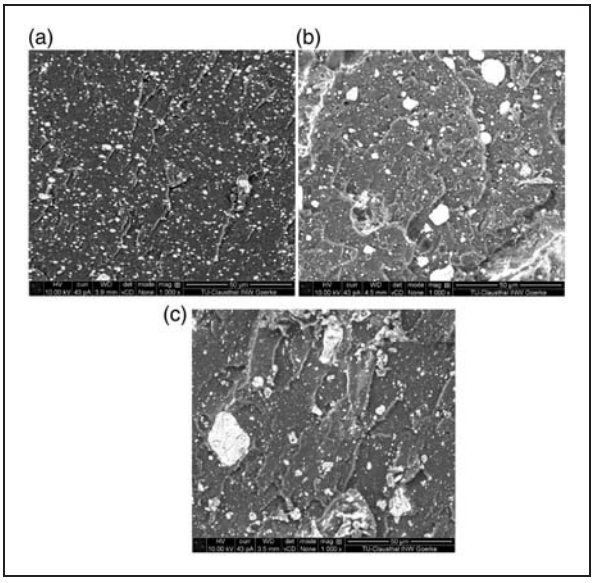

Figure 3. The SEM picture of PMMA/Fe_3O_4 nanocomposites (1000×). (a) *in situ* process. (b) in-between process. (c) *ex situ* process.

β is the peak width of half-maximum, and θ is the Bragg diffraction angle.

Based on the testing results, the *in situ*-prepared composites have the larger peak width than the *ex situ* prepared composites, which means the crystal size of Fe_3O_4 nanoparticles in the *in situ* composites is smaller than that in *ex situ* composites (D for *in situ* composite is about 20 nm). The crystal size of the Fe_3O_4 particles in the composites prepared by *in-between* process is smaller than that of *ex situ* composites but larger than that of *in situ* composites. This can be explained by the increased particle agglomeration taking place in *ex situ*-processed composites, which is confirmed by SEM microscopic tests, shown in Figure 3, in which it can be

clearly found that the composites prepared by *in situ* process attribute to best nanoparticles dispersion in the matrix and less agglomerations, whereas the *ex situ* process causes more and larger agglomerations of the particles.

Thermal properties analysis

In differential scanning calorimetric (DSC) analysis, a nitrogen atmosphere and Hermetic sealed aluminium pans were used to avoid oxidation. The specimens were measured in DSC instrument by a heat-cool-heat process. Firstly, the samples were heated from room temperature to 250°C at a rate of 10°C/min, and then at the same rate cooled down to 30°C. Afterwards, the second heat scan cycle was followed.

The DSC measuring results displayed in Figure 4 indicate that the glass transition temperature of PMMA was reduced by adding the Fe_3O_4 nanoparticles, which is regarded as the result from the reduced molecular weight and chain length of PMMA due to restriction and separation of nanoparticles on polymer molecular. The summarized DSC testing results are listed in Table 1.

Thermal degradation of PMMA and Fe_3O_4 concentrations in magnetic PMMA/Fe_3O_4 nanocomposites were identified by means of thermo gravimetric analysis (TGA) at heating rate of 10°C/min from room temperature to 600°C under the nitrogen atmosphere.

The TGA characterizing results (in Figure 5) show that the starting decomposition temperature of PMMA is reduced by adding Fe_3O_4 nanoparticles. And compared with the neat PMMA material, the thermal degradation of PMMA in PMMA/Fe_3O_4 composites occurs at lower temperature but with relative slower degradation speed. The offset temperature of decomposition of *in situ* and *in-between* composites is slightly higher than that of *ex situ*, which results from the improved homogeneous particle distribution and improved adhesion between particles and polymer matrix by compatible function of oleic additives in *in situ* and *in-between* composites.

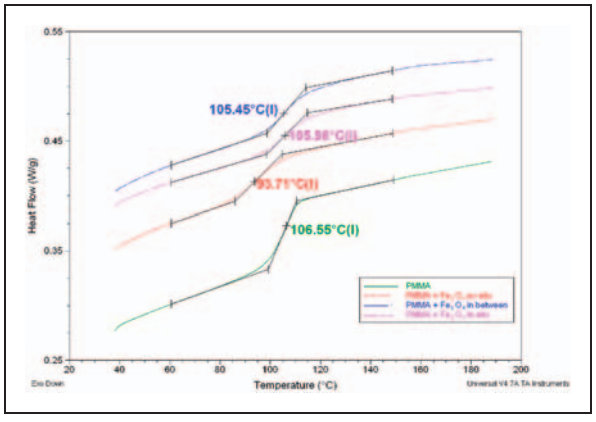

Figure 4. DSC patterns of the PMMA/Fe_3O_4 nanocomposites prepared by different methods.

Table 1. DSC measurements for various composites.

Materials	PMMA	*Ex situ*	In-between	*In situ*
Tg (°C)	106.55	93.71	105.45	105.98

Mechanical analysis

The samples for tensile tests were prepared by injection molding process on an injection molding machine Arburg 220S with a screw diameter of 15 mm and maximum clamping force of 150 kN.

Tensile test was performed on a universal mechanical test machine from Zwick Roell and tensile specimen according to the EN ISO Standard 527-2:1996. A 2.5 kN tensile load cell and 5 mm/min tensile speed were used during the tests.

As can be seen in Figure 6, the *in situ* composites show higher stiffness than *ex situ* composites. Caused by the less dispersion and increased affinity to particle agglomeration, the stiffness reinforcing effect of nanoparticles in the *ex situ* composites is weakened, which results in lower Young's modulus. Typically, the tensile strength of the polymer will be reduced dramatically by adding high contents of nanoparticles because of the reduced strength of the discontinuous fillers compared to the polymer matrix. However, the tensile strength of the *ex situ* composites is not significantly deteriorated since the particles are not well distributed in the polymer matrix.

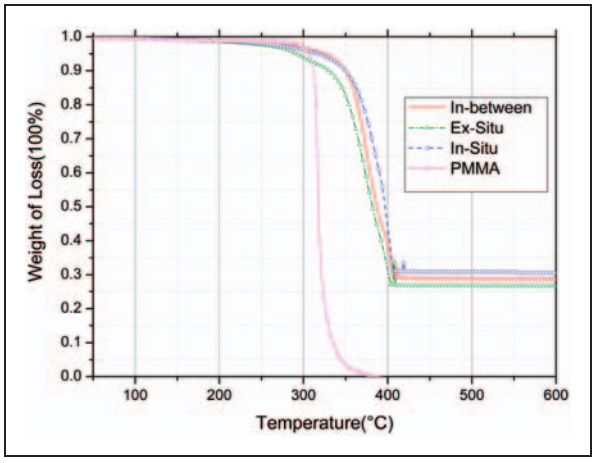

Figure 5. TGA testing results of the PMMA/Fe_3O_4 nanocomposites prepared by different methods.

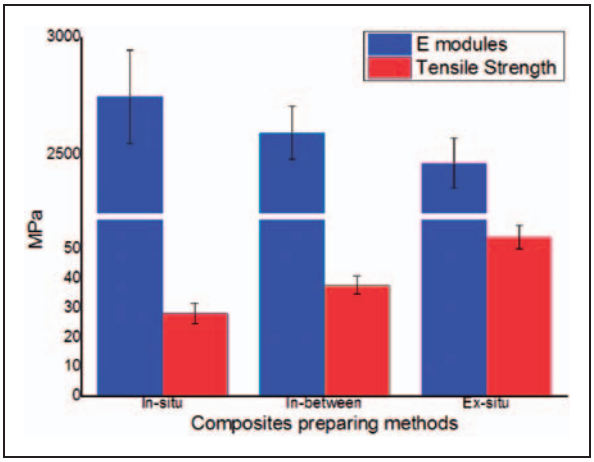

Figure 6. Tensile test results of PMMA/Fe_3O_4 nanocomposites prepared by *in situ*, *ex situ* and in-between processes.

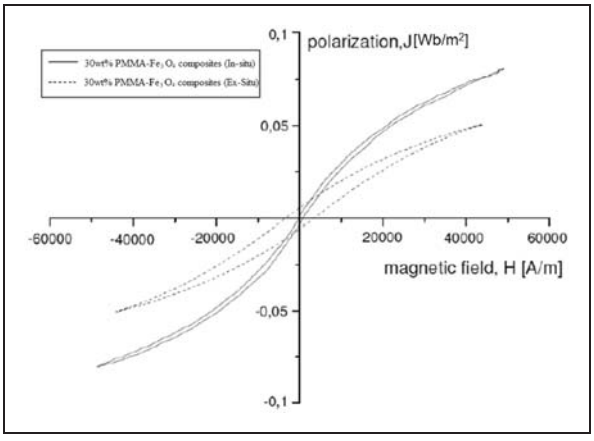

Figure 7. Hysteresis loops of *in situ* and *ex situ* prepared PMMA/Fe_3O_4 nanocomposites at the frequency of 1 Hz.

Magnetic properties

The magnetic properties of the compounded composites were evaluated as well (in Figures 7 and 8). The *in situ* prepared materials have less hysteresis loss than the one of *ex situ*. In addition, because of the polymer insulation between magnetic particles, the polymer bonded magnetic composites will be inducted less in the magnetic fields and produce less Joule heats with less eddy losses. The better dispersion of the particles in the matrix will lead to the better polymer insulation of the magnetic particles which will give better eddy's loss performance as well as the hysteresis loss performance. Therefore, according to the morphologic analysis, the *in situ* composites with better particle dispersions will have less hysteresis losses than *ex situ* composites. The same trend can be seen in the maximum saturation flux. In addition, the composites prepared by *in-between* process show higher saturation flux density

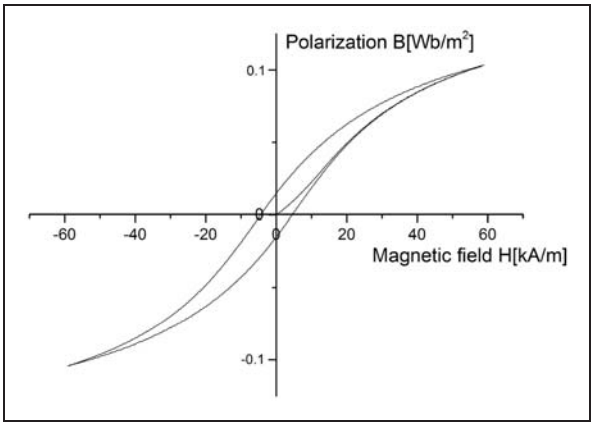

Figure 8. Hysteresis loops of in-between prepared PMMA/Fe_3O_4 nanocomposites at the frequency of 1 Hz.

than *ex situ* composites but similar hysteresis losses. However, in general, the permeability of the composites is lower than 20, which is not enough for the normal power transmission equipment; nevertheless they are most favorable candidates for high-frequency power electric and electronic applications.

Conclusions

In the presented study, the PMMA/ Fe_3O_4 nanocomposites were prepared by three different compounding processes of *in situ*, *ex situ* and in-between methods, and their mechanical, thermal and magnetic properties were characterized and analyzed. According to the achieved results, the following conclusion can be drawn:

a. The compounding principles significantly influence the thermal, mechanical and magnetic properties of magnetic PMMA/Fe_3O_4 nanocomposites.
b. The composites prepared by *in situ* methods show in general better thermal, mechanical and magnetic performance compared with *ex situ* and in-between processes.
c. However, the studied *in situ* method is not able to prepare extremely high filled magnetic nanocomposites (maximum 60 wt.%), which results in relative low magnetic flux density and magnetic permeability.

In future, works on *in situ* process with various polymer matrix and magnetic fillers should be done.

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